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(54) **High temperature, lead-free, tin based solder composition.**

(57) Disclosed is a lead-free, high solidus temperature, high Sn alloy. The solder alloys contain in excess of 90 weight percent Sn, and an effective amount of Ag and Bi, optionally with Sb or with Sb and Cu. Another form of the alloy contains Ag and Sb, optionally with Bi.

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The present invention relates to lead free, low toxicity solder alloys that are particularly useful in microelectronic applications. The solder alloys of the invention, which contain in excess of 90 weight percent Sn, and an effective amount of either (1) Ag and Bi, optionally with Sb or with Sb and Cu, or (2) Ag and Sb, optionally with Bi. These alloys are particularly useful in joining integrated circuit chips to chip carriers and substrates, as printed circuit boards, joining chip carriers to substrates, and joining circuitization lands and pads in multilayer printed circuit boards.

Background of the Invention

Soldering is a low temperature, generally reversible, metallurgical joining process. Low temperature and reversibility are especially important in electronics applications because of the materials involved and the necessity for reworking and making engineering changes.

Solder joining is a wetting process followed by a chemical reaction. Molten solder wets selectively. The selective wettability of solders allow molten solder to be confined to desired sites. This is especially important in flip chip bonding, and in working with solder masks.

The soldering process can be accomplished as quickly as the wetting takes place, for example, on the order of a few seconds. This makes soldering particularly desirable for automated, high speed, high throughput processes.

Wettability is also a function of the materials to be joined, with Cu, Ni, Au, and Pd, as well as alloys rich in one or more of these metals, being particularly amenable to soldering.

The chemical reaction following wetting is between the molten solder and the joining metallurgy to form an intermetallic phase region at the interface. The intermetallic phases formed by solders in electronic packaging are stoichiometric compounds, typically binary compounds, and typically containing Sn if Sn is present in the solder alloy. When the base, pad, or land is Cu, and the solder alloy is rich in Sn, the intermetallic formed during soldering is Cu-Sn. Exemplary Cu-Sn binaries include  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$ .

Solder alloys are characterized by the melting temperature being a strong function of composition. While a pure metal is characterized by a single, invariant, melting temperature, the freezing and melting points of alloys are complex. The freezing point of an alloy is determined by the liquidus line. Above the liquidus line only a liquid phase or phases can exist. The melting point of an alloy is determined by the solidus line. Below the solidus line only a solid phase or phases can exist. In the region between these two lines, i.e., between the liquidus line and the solidus line, solid and liquid phases can co-exist.

The preferred soldering alloys are eutectics, that is, they are characterized by a eutectic point. The eutectic point is where the liquidus and solids lines meet. A concentration change in either direction from the eutectic results in an increase in the liquidus temperature.

The composition, and the quench rate, also determine the microstructure and the resulting mechanical properties of the solder joint. Thus, it is necessary to both carefully choose the solder composition and to carefully control the thermal exposure of the soldered joint.

A solder composition used in electronics fabrication must be wettable as a solder alloy, and have at least one component capable of forming an electrically conductive, thermally stable, non-brittle, plastic intermetallic with the pad or land metallurgy. For this reason, the most common solder alloys are lead based alloys, as Sn-Pb alloys.

Heretofore, Pb/Sn solders have been utilized for electronic applications. There have been many historical reasons for the wide spread use of Pb/Sn alloys. These historical reasons include the low solidus temperature of Pb/Sn solder alloys, the workability of Pb/Sn alloys and of the resulting Cu/Sn intermetallics (formed at the solder/Cu contact interface) over a wide temperature range, the adhesion of Cu/Sn intermetallics obtained from Pb/Sn alloys to Cu lands and pads, and the ready availability of process equipment and low cost adjuncts, as resins, fluxes, and solder masks, for Pb/Sn alloys.

The relatively low temperatures required for processing Pb/Sn solder alloys are particularly important when polymeric dielectrics are used in the fabrication of electronic packages. These polymers can degrade in high temperature assembly operations. Solder alloys which melt at relatively low temperatures can accommodate these polymeric substrates.

Additionally, semiconductor chips are subject to thermal diffusion and structural transformations at elevated temperatures. Low melting solders avoid these problems.

Especially important is the "softness" or plasticity of lead based solders. This softness or plasticity allows the solder to accommodate the mismatch in coefficients of thermal expansion between the bonded structures, for example the mismatch in coefficient of thermal expansion between a ceramic

dielectric and a polymeric dielectric, or between a semiconductor chip and a ceramic or polymeric chip carrier or substrate.

However, lead is a toxic, heavy metal with a relatively high vapor pressure. Its use is disfavored, and a need exists for a replacement.

5 Various lead-free solder alloys are described in the following documents.

K.S. Subramanian et al, "Leaching of Antimony, Cadmium, Copper, Lead, Silver, Tin, and Zinc from Copper Piping With Non-Lead-Based Soldered Joints," J. Environ. Sci. Health, Vol. A26, No. 6, pp. 911-929 (1991) describes tests on the leaching of Ag, Cd, Cu, Pb, Sb, Sn, and Zn from a number of alloys. The tested alloys included 96/4 Sn/Ag, 94/6 Sn/Ag, and 95.5/4/0.5 Sn/Cu/Ag.

10 U.S. Patents 4,643,875 and 4,667,871 to Howard Mizuhara for TIN BASED DUCTILE BRAZING ALLOYS describe high temperature brazing alloys containing from 35% to 95% Sn, from 0.5 to 70% Ag, from 0.5 to 20% Cu, effective amounts of one or more of Ti, V, and Zr, and optionally with Ni, and Cr. The disclosed brazing alloys all require temperatures of at least 550 degrees Celsius for good bonding.

U.S. Patent 4,778,733 to Lubrano et al for LOW TOXICITY, CORROSION RESISTANT SOLDER  
15 describes an article of manufacture, as a plumbing fixture, containing from 92 to 99% Sn, from 0.7 to 6% Cu, and from 0.05-3% Ag.

USP 4,797,328 to Boehm et al for SOFT-SOLDER ALLOY FOR BONDING CERAMIC ARTICLES describes soft-solder alloys for bonding ceramic parts without premetallization. The alloys, which are disclosed to be useful for bonding alumina parts to copper parts, contain from 86 to 99% Sn, from 0 to 13%  
20 Ag and/or Cu, from 0 to 10% In, and from 1 to 10% Ti.

USP 4,806,309 to Stanley Tulman for TIN BASE LEAD-FREE SOLDER COMPOSITION CONTAINING BISMUTH, SILVER, AND ANTIMONY describes solder compositions containing from 90 to 95% Sn, from 3 to 5% Sb, from 1 to 4.5% Bi, and from 0.1 to 0.5% Ag. Tulman describes the use of Bi to lower the melting point of the solder to about 425 degrees F (218 degrees C).

25 USP 4,929,423 to K.L. Tucker and U. Ma for LOW TOXICITY ALLOY COMPOSITIONS FOR JOINING AND SEALING describes a lead-free solder alloy, described as being useful for plumbing, contains from 0.08 to 20% Bi, from 0.02 to 1.5% Cu, from 0.01-1.5% Ag, up to about 0.10% P, up to about 0.20% Rare Earth, and balance (ca. 80%) Sn.

### 30 Objects of The Invention

It is a primary object of this invention to provide a lead free solder.

It is a further object of this invention to provide a lead free solder that wets and forms a chemically and thermally stable intermetallic with the bonding metallurgy typically used in electronics fabrication, e.g., Cu,  
35 Au, Ag, and Pd, especially while avoiding wetting organic materials as substrates and solder masks.

It is a further object of this invention to provide a lead free solder having that flows at low enough temperatures to avoid damage to electronic materials.

### Summary of the Invention

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These and other objects of the invention are obtained, and the shortcoming of the art are overcome by the lead-free, high solidus temperature, high service temperature, high strength multi-component solder alloys of the invention.

In one embodiment of the invention the alloy contains at least about 90 weight percent Sn, with  
45 effective amounts of Ag, and Bi for thermal stability and strength. In a further exemplification of this embodiment of the invention the alloy contains Sb, and in a still further exemplification the alloy contains Sb and Cu.

In a further embodiment of the invention, the high solidus temperature, high service temperature, high strength multi-component solder alloy. The alloy contains at least about 90 weight percent Sn and effective  
50 amounts of Ag, and Sb. Additionally, a small amount of bismuth may be present in the alloy.

### DETAILED DESCRIPTION OF THE INVENTION

These and other objects of the invention are obtained, and the shortcoming of the art are overcome by  
55 the lead-free, high solidus temperature, high service temperature, high strength multi-component solder alloys of the invention.

In one embodiment of the invention the alloy contains at least about 90 weight percent Sn, with effective amounts of Ag, and Bi for thermal stability and strength. One such alloy contains about 95.0 to

95.5 weight percent Sn, about 2.5 to 3.0 weight % Ag, and about 2.0 weight % Bi.

In a further exemplification of this embodiment of the invention the alloy contains Sb. One alloy, according to this exemplification of the invention contains about 93.5 to about 94.0 weight % Sn, about 2.5 to about 3.0 weight % Ag, about 1.0 to about 2.0 weight percent Bi, and about 1.0 to about 2.0 weight percent Sb.

In a still further exemplification the alloy contains Sb and Cu. One particularly preferred Sn-Ag-Sb-Cu alloy is an alloy containing about 93.5 to about 94.0 weight % Sn, about 2.5 to about 3.0 weight % Ag, about 1.0 to about 2.0 weight percent Bi, about 1.0 to about 2.0 weight percent Sb, and about 1.0 weight percent Cu.

In a further embodiment of the invention, the high solidus temperature, high service temperature, high strength multi-component solder alloy. The alloy contains at least about 90 weight percent Sn and effective amounts of Ag, and Sb. One such high Sn alloy contains about 94.0 to 95.0 weight percent Sn, about 2.5 to 3.5 weight % Ag, and about 2.0 weight % Sb.

Additionally, a small amount of bismuth may be present in the alloy. One such high Sn alloy contains about 93.5 to about 94.0 weight % Sn, about 2.5 to about 3.0 weight % Ag, about 1.0 to about 2.0 weight percent Bi, and about 1.0 to about 2.0 weight percent Sb.

The solder alloy compositions of the invention are summarized in the Tables below:

Component	Content (weight %)
Sn	95.0 to 95.5 weight %
Ag	2.5 to 3.0 weight %
Bi	appx 2 weight %
Additive Component	Content (weight %)
Sb	93.5 to 94 weight % Sn 2.5 to 3 weight % Ag appx 2 weight % Bi 1.0 to 2.0 weight % Sb
Sb + Cu	93.5 to 94 weight % Sn 2.5 to 3 weight % Ag 1 to 2 weight % Bi 1.0 to 2.0 weight % Sb appx 1 weight % Cu

and

Component	Content (weight %)
Sn	94.0 to 95.0 weight %
Ag	2.5% to 3.5% Ag
Sb	appx 2 weight % Sb
Additive Component	Content (weight %)
Bi	93.5 to 94.0 weight % Sn 2.5 to 3.0 weight % Ag 1.0 to 2.0 weight % Sb 1.0 to 2.0 weight % Bi

According to one preferred embodiment of the invention there is provided a method of electrically connecting an integrated circuit chip to a circuitized substrate. This interconnection method includes the step of depositing a solder alloy comprising at least about 90 weight percent Sn and either

(1) effective amounts of Ag, and Bi (for example, about 95.0 to 95.5 weight percent Sn, about 2.5 to 3.0 weight % Ag, and about 2.0 weight % Bi), optionally with Sb, and further, optionally, with Cu; or

(2) effective amounts of Ag and Sb (for example about 94.0 to 95.0 weight percent Sn, about 2.5 to 3.5 weight % Ag, and about 2.0 weight % Sb) optionally with Bi, onto electrical contacts of the integrated circuit chip. The solder alloy may be applied by wave solder deposition, electrodeposition, or as a solder paste.

5 The electrical leads of the circuitized substrate are then brought into contact with the solder alloy on the electrical contacts of the integrated circuit chip. Where the chip is to be mounted in a "flip chip" conformation, the current leads of the circuitized substrate are pads on the substrate, and the solder alloy deposits are brought into contact with the pads. Alternatively, where the integrated circuit chip is mounted right side up, the current leads are wire leads, and tab inner lead connections, and they are brought into  
10 contact with the solder alloy contacts on the top surface of the integrated circuit chip.

While the substrate current leads and the solder deposits are maintained in contact the solder alloy is heated to cause the solder alloy to wet and bond to the electrical leads of the circuitized substrate. Heating may be by vapor phase reflow, infrared reflow, laser reflow, or the like.

The resulting microelectronic circuit package of the invention is an integrated circuit chip module with a circuitized chip carrier, i.e., a substrate, a semiconductor integrated circuit chip, and a solder bond electrical  
15 interconnection between the circuitized chip carrier and the semiconductor integrated circuit chip formed of a solder alloy comprising at least about 90 weight percent Sn and either

- (1) effective amounts of Ag, and Bi (for example, about 95.0 to 95.5 weight percent Sn, about 2.5 to 3.0 weight % Ag, and about 2.0 weight % Bi), optionally with Sb, and further, optionally, with Cu; or  
20 (2) effective amounts of Ag, and Sb (for example about 94.0 to 95.0 weight percent Sn, about 2.5 to 3.5 weight % Ag, and about 2.0 weight % Sb) optionally with Bi.

The invention may be understood by reference to the following examples.

#### Examples

##### Example I

Five sample alloys were prepared, applied, and tested. The alloys had the compositions shown in the tables below.

Alloy	Sn	Ag	Sb	Bi	Cu
1	93.0	3.0			4.0
2	95.0	3.0	2.0		
3	93.0	3.0	2.0	2.0	
4	95.0	3.0		2.0	
5	95.5	2.5		2.0	

##### Example II

45 A series of 95 weight percent Sn - 3 weight percent Ag - 2 weight percent Sb solder alloys were prepared and tested for various solder properties.

In another test the alloys were tested to determine their creep properties. The tensile strength of the alloy showed a projected rupture time of 70 days at 2500 psi and 23 degrees Centigrade.

The tensile strength was measured to be 59 (100 lbs/sq. inch), the yield strength was measured to be 31 (100 lbs/square inch), and the percent elongation was measured to be 35 percent.  
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The melting point of the alloy was measured to be 218 to 255 degrees Celsius.

##### Example III

55 A series of 93 weight percent Sn - 3 weight percent Ag - 2 weight percent Sb - 2 weight percent Cu solder alloys were prepared and tested for various solder properties.

In another test the alloys were tested to determine their creep properties. The tensile strength of the alloy showed a projected rupture time of 70 days at 2500 psi and 23 degrees Centigrade.

The alloys were also tested for cycle fatigue at 4.3 percent deflection at 23 degrees Celsius and five cycles per minute. Failure occurred after 60 cycles.

The melting point of the alloy was measured to be 200 to 224 degrees Celsius.

## 5 Claims

1. A high solidus temperature, high service temperature, high strength multi-component solder alloy comprising at least about 90 weight percent Sn and the balance comprising Ag, and Bi.
- 10 2. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 1 comprising about 95.0 to 95.5 weight percent Sn, about 2.5 to 3.0 weight % Ag, and about 2.0 weight % Bi.
- 15 3. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 1 further comprising Sb.
- 20 4. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 3 comprising about 93.5 to about 94.0 weight % Sn, about 2.5 to about 3.0 weight % Ag, about 1.0 to about 2.0 weight percent Bi, and about 1.0 to about 2.0 weight percent Sb.
- 25 5. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 3 further comprising Cu.
6. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 3 comprising about 93.5 to about 94.0 weight % Sn, about 2.5 to about 3.0 weight % Ag, about 1.0 to about 2.0 weight percent Bi, about 1.0 to about 2.0 weight percent Sb, and about 1.0 weight percent Cu.
- 30 7. A high solidus temperature, high service temperature, high strength multi-component solder alloy comprising at least about 90 weight percent Sn and the balance comprising Ag, and Sb.
8. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 7 comprising about 94.0 to 95.0 weight percent Sn, about 2.5 to 3.5 weight % Ag, and about 2.0 weight % Sb.
- 35 9. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 8 further comprising Bi.
- 40 10. The high solidus temperature, high service temperature, high strength multi-component solder alloy of claim 9 comprising about 93.5 to about 94.0 weight % Sn, about 2.5 to about 3.0 weight % Ag, about 1.0 to about 2.0 weight percent Bi, and about 1.0 to about 2.0 weight percent Sb.
- 45 11. A method of electrically connecting an integrated circuit chip to a circuitized substrate comprising the steps of:
  - a. depositing a solder alloy according to any one of claims 1 to 6 or 7 to 10 onto electrical contacts of the integrated circuit chip;
  - b. bringing electrical leads of the circuitized substrate into contact with the solder alloy on the electrical contacts of the integrated circuit chip; and
  - c. heating the solder alloy to cause the solder alloy to wet and bond to the electrical leads of the circuitized substrate.
- 50 12. The method of claim 11 wherein the electrical leads of the circuitized substrate are chosen from the group consisting of pads, wire leads, and tab inner lead connections.
- 55 13. An integrated circuit chip module comprising a circuitized chip carrier, a semiconductor integrated circuit chip, and a alloy electrical solder bond interconnection according to claim 1 between said circuitized chip carrier and said semiconductor integrated circuit chip.

14. An integrated circuit module comprising a circuitized chip carrier, a semiconductor integrated circuit chip, and a alloy electrical solder bond interconnection according to claim 7 between said circuitized chip carrier and said semiconductor integrated circuit chip.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 94 10 8683

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	CHEMICAL ABSTRACTS, vol. 81, no. 18, 4 November 1974, Columbus, Ohio, US; abstract no. 110264, TAGUCHI, TOSHIHIKO ET AL 'Tin alloy for high-temperature solder' * abstract * & JP-A-49 038 858 (TAGUCHI, TOSHIHIKO;KATO, KIKIYA) ---	1-10	B23K35/26 C22C13/00 H05K3/34
X	IBM TECHNICAL DISCLOSURE BULLETIN, vol.23, no.8, January 1981, NEW YORK US page 3620 O.I.CHIRINO ET AL 'High creep strength alloy' ---	1-10	
X	GB-A-1 181 198 (ROBERT BOSCH)  * claims 1,6 * ---	1,3,7,9, 11,13	
X	US-A-4 170 472 (D.R.OLSEN ET AL)  * column 2; table * ---	7,8,11, 13	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
X	WELDING PRODUCTION, vol.29, no.5, May 1982, CAMBRIDGE GB pages 17 - 18 B.S.LISITSKII ET AL 'Effect of alloying additions on the properties of soldering alloys based on tin.' * the whole document * ---	7	B23K C22C H05K
A	EP-A-0 354 392 (HITACHI) ---		
A	US-A-4 879 096 (P.E.NATON) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 September 1994	Examiner Mollet, G
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			